Tuning the Properties of Carbon Nanotubes by Deformation

Carbon nanotubes continue to surprise scientists with their novel properties. Recently we have discovered many intimate relationships between structural deformation and the properties of single-walled nanotubes (SWNT) that could be important in technological applications [1, 3]. These observations were made using state-of-the-art first-principles total energy calculations within the pseudo-potential and the generalized gradient approximations (GGA). Here we present a brief review of our findings.

SWNTs are basically rolled graphite sheets which are characterized by two integers (*n,m*) defining the rolling vector of graphite. Therefore, the electronic properties of SWNTs, to first order, can be deduced from that of graphite by mapping the band structure from a 2D hexagonal lattice onto a cylinder. Such an analysis indicates that (*n,n*) "arm-chair" nanotubes are always metallic and (*n,0*) zigzag nanotubes are metallic only if *n* is an integer multiple of three. From our first-principles calculations we find that these electronic properties can be significantly modified by radial strain, which distorts the circular cross section to an elliptical one.

Figure 1 shows that the energy gap of an insulating SWNT decreases and eventually vanishes at an insulator-metal transition with increasing applied elliptical strain. The density of states at the Fermi level $N(E_F)$, of a metallized SWNT increases with increasing deformation. More interestingly, the elliptical deformation necessary to induce metallicity is found to be in the elastic range. Therefore, all strain induced changes in electronic and also in mechanical properties are reversible.

Another significant effect of the elliptical distortion of SWNTs is the change in the uniformity of their charge distribution. This, in turn, imposes changes in the chemical reactivity and hence on the interaction of the tube surface with foreign atoms and molecules. To demonstrate this, we calculate the binding energies of H and a simple metal atom, Al, on SWNTs as functions of nanotube radius (R), type, and elliptical deformation. We find that the binding energy, E_B, is positive (i.e., stable) and follows a remarkably simple $1/R$ scaling for (*n,0*) SWNTs for both H and Al, even though H prefers to sit on top of C atoms and Al favors the hollow sites (i.e., top of hexagons). Increasing binding energy with

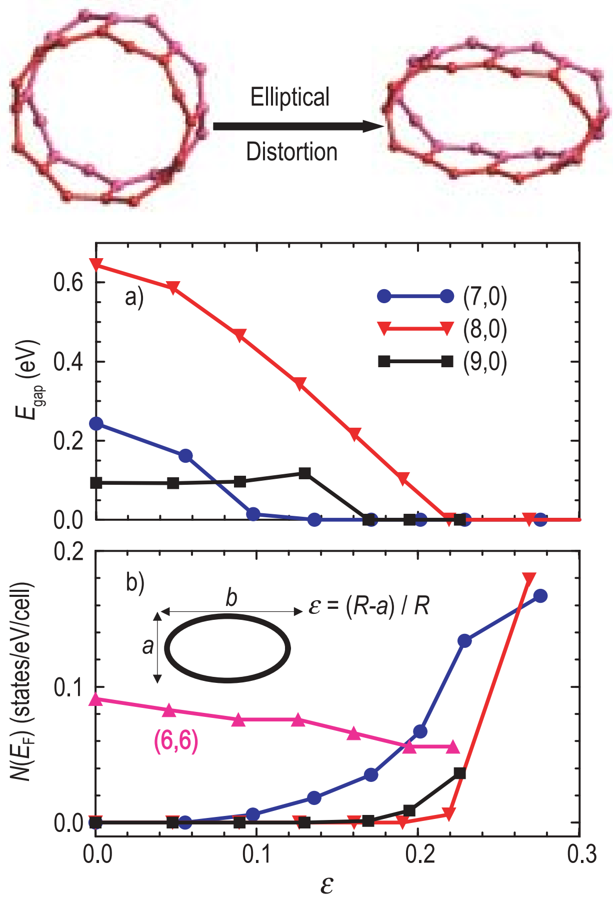

FIGURE 1. Variation of the energy band gap E_{gap} (a) and density of the states at the Fermi energy (b) as a function of elliptical deformation.

increasing curvature (i.e., decreasing R) suggests that E_B can be modified by elliptical deformation.

Figure 2 shows the variation of the binding energy E_B of a single hydrogen atom adsorbed on the sharp and flat edges of the (8,0) surface with elliptical distortion. With increasing distortion, the binding energy of the sharp site increases, while it decreases for the flat site, creating an energy difference of ≈ 1.1 eV at the distortion value $\varepsilon = 0.3$. This value is 44 % of the binding energy of H on the undeformed SWNT.

The binding energy of Al exhibits a behavior similar to that of H, despite H and Al favoring different sites on the (8,0) tube. Elliptical deformation increases the binding energy of both the flat and sharp sites for Al, given an energy difference of 0.5 eV at the deformation $\varepsilon = 0.3$. It is

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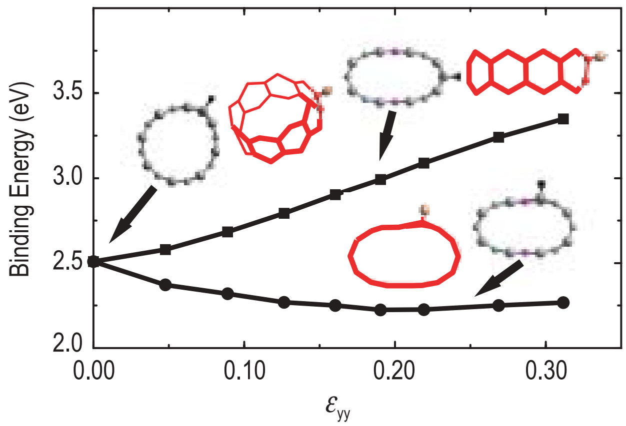

FIGURE 2. Binding energies of the sharp (top) and the flat sites (bottom) versus elliptical deformation for a hydrogen adsorbed on a (8,0) SWNT.

remarkable that Al, which is not bound to the graphite, can be adsorbed at the sharp site of the distorted SWNT with a binding energy of 1.8 eV. Hence, we conclude that not only band gap engineering but also chemical reactions taking place on the surface of a SWNT can be engineered through radial deformation.

Explanation of this remarkable change of the binding energy with elliptical deformation is sought in the electronic structure of SWNTs. Figure 3 shows the response of the first conduction band to elliptical distortion. It is clear that the distortion disturbs the uniformity of the charge distribution of the SWNT and pushes the chemically most active electrons from the flat to the sharp site of the nanotube, increasing the adsorption energy of the sharp site significantly. Surprisingly the effect of distortion on metallic armchair (*n,n*) nanotubes is found to be very small due to the metallic bands of the tubes [2]. This could be important in selective functionalization of nanotubes. See Ref. 1 for animation of this effect.

We believe that the tunable electronic and chemical properties reported here can have important implications for metal coverage and for selective adsorption and desorption of atoms and molecules on carbon nanotubes. This could allow the fine tuning of the properties of SWNTs via reversible deformation and can ultimately lead to a wide variety of technological applications such as variable metal-insulator junctions, quantum wells, catalysts, hydrogen storage devices, magnetic tubes (by absorbing magnetic ions), etc.

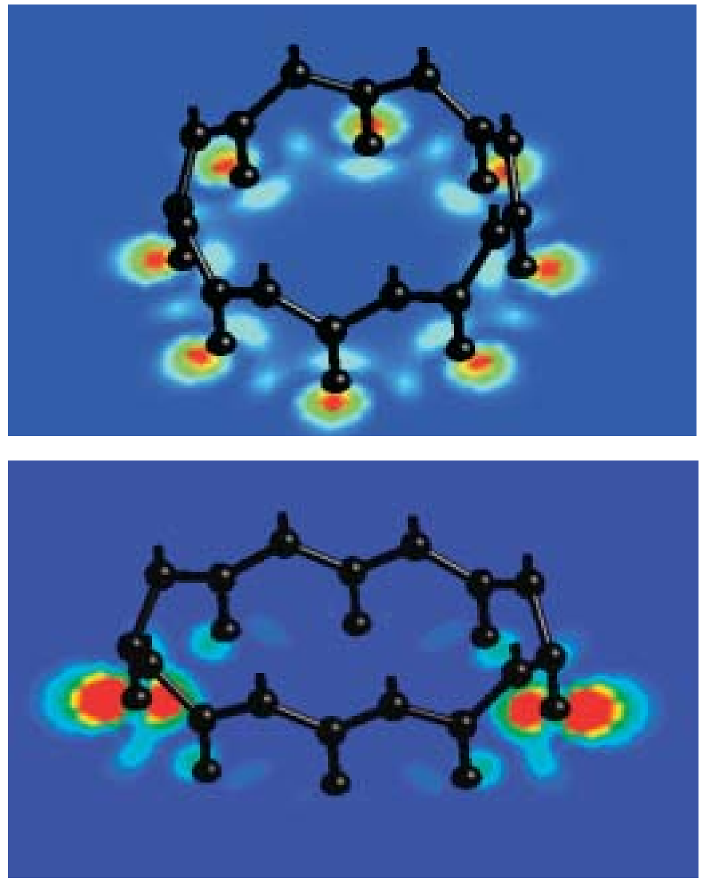

FIGURE 3. Contour plot of the first conduction band of an undeformed (top) and elliptically deformed (bottom) (8,0) SWNT. See Ref. 1 for animation of this effect.

References

[1] See http://www.ncnr.nist.gov/staff/taner/nanotube.

[2] O. Gulseren, T. Yildirim, and S. Ciraci, Phys. Rev. Lett. **87**, 116802 (2001).

[3] C. Kilic, S. Ciraci, O. Gulseren, and T. Yildirim, Phys. Rev. **B62**, R16345 (2000).